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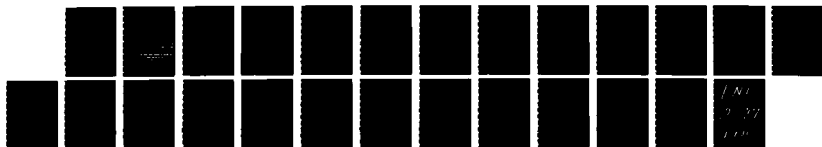
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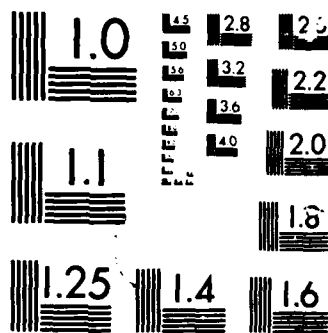
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TECHNICAL REPORT ARAED-TR-86028

**NMR INVESTIGATIONS OF LIQUID PROPELLANT SYSTEMS
CONSISTING OF ALKYL- AND HYDROXYLAMMONIUM NITRATES**

**PART 2. MEASUREMENT OF CARBON-13 SPIN-LATTICE RELAXATION
TIMES AND ACTIVATION ENERGIES FOR MOLECULAR MOTION IN
MODEL LIQUID PROPELLANT SYSTEMS**

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4. Title: PART 2. MEASUREMENT OF CARBON-13 SPIN-LATTICE RELAXATION TIMES AND ACTIVATION ENERGIES FOR MOLECULAR MOTION IN MODEL LIQUID PROPELLANT SYSTEMS

20. Abstract (cont):

of ion pairing, ion clustering, molecular associations, and reorientations.

The carbon-13 data lead to the conclusion that it is essential to study the nitrogen spin-lattice relaxations at the charge sites in the alkyl- and hydroxylammonium nitrates to get a better understanding of the motional dynamics, solvation effects, and ion clustering phenomena. Studies with nitrogen-15 labeled compounds are proposed.

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INTRODUCTION

The characterization of carbon-13, proton, and nitrogen-15 NMR spectra of four alkyl ammonium nitrates (AAN's) which are potential candidates for HAN (hydroxylammonium nitrate)-based liquid propellants and their analytical applications are described in Part 1 of this report (ref 1). The efforts made thus far to study the molecular motion and ionic interactions such as ion pairing in the same systems [namely, IPAN (isopropylammonium nitrate), TEAN (triethanolammonium nitrate), TMAN (trimethylammonium nitrate) and NBAN (n-butylammonium nitrate)], employing NMR relaxation methods, are summarized here in Part 2. Similar but more extensive studies on some n-butyl ammonium salts other than the nitrate were previously reported in the literature by Levy and coworkers (ref 2, 3).

The primary purpose of the NMR work described here was to study the microstructure and ionic interactions in the highly concentrated aqueous liquid propellants. The measurement of carbon-13 spin-lattice relaxation times (T_1 's) is a well known experimental approach for this study since these values are generally dependent on the distribution of motional frequencies of the molecules in a sample. Furthermore, the relaxation data relate to the bonded and nonbonded interactions which affect molecular motions. In ionic solutions which the liquid propellants represent, the carbon-13 T_1 's relate directly to the microscopic motions of the ions enabling one to study solution effects such as solvation of ions, ion pairing, and aggregation.

Also included in this report are the nuclear Overhauser enhancements (NOE's) which suggest that the predominant spin-lattice relaxation mechanism in these systems is the dipolar interaction, as well as the temperature dependences of T_1 's from which the activation energies for the molecular reorientation processes were derived.

Theory and Significance of the Spin-Lattice Relaxation Times

Spin-lattice relaxation is the process by which the nuclear spins, following the excitation pulse, transfer energy to the surrounding molecular network in the liquid or solid commonly referred to as "lattice." For efficient transfer of energy, a mechanism of coupling between the nuclear spins and the molecular lattice is necessary. In all the well-known mechanisms (ref 4), the presence of fluctuating local magnetic fields near the relaxing nucleus caused by molecular tumbling provides that coupling. In molecules containing quadrupolar nuclei (spin $> 1/2$) such as nitrogen-14, interactions between the nuclear spin and the electric field gradient at the nucleus also provide a relaxation mechanism as the molecule reorients. Generally, for protonated carbons, the magnetic dipole-dipole interactions dominate the spin-lattice relaxation mechanisms.

Another mechanism which may contribute to the spin-lattice relaxation in the liquid propellant systems under study is the spin-rotation relaxation. This is important in molecules containing highly symmetrical groups such as a methyl or a short, aliphatic chain capable of intramolecular segmental motions. Paramagnetic relaxation, which may also be relevant to the liquid propellants, arises from dissolved oxygen or other paramagnetic impurities in a sample. The large

magnetic moment of electron relative to nuclear magnetic moments can provide an efficient dipolar relaxation. In addition, two other mechanisms which are only important in rare instances are the chemical shift anisotropy and scalar coupling. All of these mechanisms combine to produce an overall spin-lattice relaxation time, T_1^{obs} , given by

$$\frac{1}{T_1^{\text{obs}}} = \frac{1}{T_1^{\text{dd}}} + \frac{1}{T_1^{\text{sr}}} + \frac{1}{T_1^{\text{q}}} + \frac{1}{T_1^{\text{sc}}} + \frac{1}{T_1^{\text{csa}}}$$

A detailed discussion of the relative importance of these mechanisms is available in the literature (refs. 4 through 6), but the dipolar relaxation, which often is the principal mechanism for protonated carbons, is considered here further.

Two neighbouring magnetic nuclei placed in an external magnetic field, H_0 , will experience the interacting fields of each other superimposed on the H_0 . The strength of this "dipole-dipole interaction" depends on the magnetic moments of the two nuclei, the internuclear distance, and their mutual orientation relative to the H_0 . The following equation describes this relation more precisely for the case of C-13 and H-1 nuclei:

$$1/T_1^{\text{dd}} = N h^2 \gamma_C^2 \gamma_H^2 r_{\text{C-H}}^{-6} \tau_{\text{eff}} \quad (1)$$

In equation 1, T_1^{dd} is the dipolar spin-lattice relaxation rate, N is the number of hydrogens bonded to the carbon, γ_C and γ_H are the magnetogyric ratios of the two nuclei, $r_{\text{C-H}}$ is the C-H bond length, and τ_{eff} is an effective rotational correlation time of the C-H vector. τ_{eff} combines the effective correlation time for internal rotation (τ_i) of the C-H vector and the correlation time for the overall reorientation, τ_c , given by the relation

$$1/\tau_{\text{eff}} = 1/\tau_c + 1/\tau_i \quad (2)$$

Molecular correlation time, (τ), used to describe the molecular motions, which can be very fast or very slow, has been variously described (ref 6) as the average time between molecular collisions or the average time for a molecular rotation or vibration to take place. Dipole-dipole relaxation is most efficient with rotational motions of frequencies comparable to the resonance frequency of the nuclei under consideration. Equations 1 and 2 show that measurement of spin-relaxation times (T_1 's) yields information about molecular motions in terms of correlation times. A study of these correlation times as a function of experimental parameters such as concentration, temperature, and other interacting species would afford insights into the solution effects mentioned above.

The presence of paramagnetic species such as Cu(II) or Fe(III) will affect the spin-lattice relaxation times under discussion. At levels of 10^{-3} moles/l of

unpaired spins, electron-nuclear dipole-dipole relaxation efficiently competes with normal diamagnetic relaxation. Evidence of this can be obtained by the measurement of what is known as the nuclear Overhauser enhancement (NOE) (ref 7). In interacting nuclei, such as carbon-13's and the spin-coupled protons, perturbation of one set of spins by RF radiation promotes an increase in intensity (population) in the other set of nuclei (ref 7). Consequently, under proton-decoupling conditions the C-13 signal intensity will increase, the maximum possible magnitude of which is given by

$$\eta = 0.5 \times \frac{\gamma_{1H}}{\gamma_{13C}} = 1.987$$

where η represents the NOE and γ_{1H} and γ_{13C} are the magnetogyric ratios of proton and carbon-13, respectively. The maximum new intensity of a given peak would thus be $1 + \eta = 2.987$, relative to the intensity without proton decoupling. From the spin-lattice relaxation measurements information can, therefore, be obtained about the specific interactions in the presence of paramagnetic species relevant to the stability of the liquid propellant systems.

Measurement of Spin-Lattice Relaxation Times (T_1)

The spin-lattice relaxation time measurements of the individual carbon atoms in the liquid propellant systems studied have been made by the "inversion recovery" method (ref 6). Conceptually this technique may be understood in terms of the "rotating frame coordinate system" used (ref 6) to describe the nuclear motions. It is well known that when nuclei of spin 1/2, such as carbon-13, are placed in a magnetic field, H_0 , they will precess around the direction of the field, z-axis, with their characteristic Larmour frequency, ω_0 , in the ordinary laboratory coordinate system. If, however, the laboratory is seen as rotating at the Larmour frequency, ω_0 , around the applied field, then the nuclei would appear stationary and coincident with the magnetic field axis, z. The magnetic behavior of the nuclear spins may then be described by the bulk magnetization vector, M_0 , which is normally stationary along the z-axis. Application of a radio-frequency, ω_0 , pulse along the x-axis would then be equivalent to applying a static field, H_1 , in the rotating frame which will rotate the magnetization vector, M_0 , clockwise through y, -z, and -y back to z axes for 90-, 180-, 270-, and 360-degree pulse times, respectively. In the "inversion recovery" method, a 180-degree pulse is applied at the C-13 resonance frequency to invert the magnetization to the -z-axis. Immediately after this, the magnetization vector, M_z , relaxes back along the z-axis to the equilibrium value, M_z^0 , according to the relation

$$M_z = M_z^0 [1 - 2 \exp(-\tau/T_1)]$$

where τ is the time in seconds after the pulse and T_1 is the spin-lattice relaxation time. M_z is measured, however, after variable τ , by the application of a 90-degree pulse to tip the magnetization on to the -y or +y axis where it can be detected. After waiting next for a period of about 5 T_1 's for the magnetization

to recover fully, the cycle is repeated with a different delay (τ) . The full cycle, (180- τ -90- PD) is in fact repeated 'n' times for each τ - value to obtain a good signal-to-noise ratio and the T_1 determined graphically from the relationship

$$\ln (M_z - M_z^0) = -\ln (2M_z^0) - \tau/T_1$$

More details about this and other methods for the T_1 -measurements are available in the literature (ref 6).

EXPERIMENTAL

Materials

Samples of the four aliphatic amine nitrates (AAN's) and the hydroxylammonium nitrate, HAN (as an 80% aqueous solution), were obtained from the Ballistic Research Laboratory, Aberdeen Proving Ground, MD. All solutions used in this work were made with deionized water. No attempts were made in this phase of the work to degas the solutions free from possible dissolved oxygen.

NMR Instrumentation

All the spin-lattice relaxation times, T_1 's, were measured on a Varian XL-200 NMR spectrometer using the inversion recovery-Fourier transform, IRFT, pulse sequence with a delay of at least 5 T_1 's. The T_1 measurement for each carbon had at least seven points (τ 's) and the T_1 's were computed by the Varian-supplied software. The temperature control of samples was within $\pm 0.2^\circ\text{C}$.

The NOE's reported in this work were obtained also by Varian supplied software. The method involves acquisition of two C-13 spectra of each compound under study, identical in every respect except that one is acquired with proton decoupler on during the delay time (approximately $5 \times T_1$) prior to the C-13 pulse and the other without. In both cases the decoupler is on during spectral acquisition and a proton decoupled spectrum is obtained. But in the latter, NOE is suppressed because it is time dependent and, in the absence of decoupling during the delay time, it cannot build up and be observed. (See reference 7 for more details.) The difference in the C-13 signal intensities between the two spectra indicates the presence of NOE and their ratios are a direct measure of the NOE ($1 + \eta$) .

Activation Energies for Molecular Motions

In the case of n-butylammonium nitrate (NBAN), trimethylammonium nitrate (TMAN), and trimethylammonium chloride, the T_1 's were measured as a function of temperature and their logarithms were plotted against reciprocal temperatures, K . The activation energies were then derived from the slopes of the straight line plots obtained.

RESULTS AND DISCUSSION

The carbon-13 spin-lattice relaxation times, T_1 's, of various carbons in the three AAN's, IPAN, TEAN, AND TMAN, are summarized in table 1, which includes data at two concentrations for each and at two temperatures (20° and $50^\circ C$, respectively) for TEAN and TMAN. The T_1 's measured in the three free aliphatic amines corresponding to the three AAN's and the respective aqueous solutions are given in table 2. The T_1 's of the AAN's in the presence of HAN, in each case are summarized in table 3. The NOE's determined in most cases are included in the three tables. n-Butylamine and some of its salts have been studied in the past (refs 2 and 3). These data from the literature together with the data on NBAN studied in the present work are summarized in table 4. The T_1 's of the nitrate (NBAN) at different concentrations and temperatures and in the presence of a paramagnetic salt, $CuCl_2$, are shown in table 5. The effect of ethylenediamine tetraacetate, EDTA, which is an effective complexing agent for the Cu^{++} ions, was studied and these results are also included in table 5. The energies of activation for the molecular reorientation were measured only for NBAN, TMAN, and trimethylammonium chloride and are presented in table 6.

Comparison of the Free Alkylamines with the Nitrates and Hydroxides

Except in the case of triethanolamine which is discussed separately below, the T_1 's of the carbons in the free amines (neat) (table 2, lines 1, 5, and 8, and table 4, line 8) were found to be generally longer than those for the hydroxides (table 2, aqueous solution data) and the nitrates (table 1 and table 4, line 1). This clearly suggests that the molecular motion (tumbling rate) of the free amines is faster than for the ammonium ions. The ammonium ions may be expected to exert an anchoring effect and slow down the overall reorientation rate. A similar effect observed before in n-butylamine and its tri-fluoroacetate (ref 2) was believed to be due to electrostatic solute ordering effects and the intermolecular interactions among the ammonium ion, its counter ion, and the solvent shell (ref 2). The anchoring effect of the ammonium ion is also evident in the generation of a segmental motion in NBAN (table 5) with a moderately long chain. Among the four AAN's studied, NBAN, with a somewhat long carbon chain, was the only one expected to show evidence of segmental (end group) motion.

Triethanolamine as well as its nitrate (table 1) and hydroxide (table 2) exhibit clearly shorter C-13 relaxation times, due, presumably, to the highly possible hydrogen bonded structures and the resulting molecular association. Furthermore, the free amine gives significantly shorter relaxation times relative

to the nitrate and hydroxide contrary to the other three amines discussed above. This must mean that there is a higher degree of molecular association in the free amine possibly through intermolecular hydrogen bonding between the hydroxyl group and the nitrogen lone pair of electrons.

Concentration Effects on the Relaxation Times

In general one should observe increased correlation times and lower relaxation times as the concentration of the aliphatic ammonium ions increases (refs 2 and 3). However, in the four short chain AAN's studied in this work no such effect is apparent even with a 10-fold increase in concentration of the nitrates (tables 1 and 5) and the hydroxides (table 2). n-Butylammonium nitrate (NBAN) however, suggests a slight decrease in the relaxation times at 3.95 moles/l concentration (table 5) compared to the next lower concentration used. The possibility that the general lack of concentration might be due to ion pairing should be considered.

Relaxation Times in the Liquid Propellant Mixtures (AAN's + HAN)

The T_1 's of the carbons in all the AAN's are generally shorter when mixed with HAN (table 3). This could be accounted for by a possible increase in viscosity of the solutions, which should also be related to the ion association or clustering due to the OH group in the HAN and the consequent slower reorientation rates.

Temperature Effects

The data in tables 1 and 5 show the T_1 's measured at two temperatures for some of the nitrates. The T_1 's, not surprisingly, increase with temperature in every case due to the expected greater mobility of the solute molecules.

Role of the Anions

The data (table 4) on several salts of n-butylamine were largely taken from the literature (ref 1 and 8) with the exception of the measurements on the nitrate (NBAN) which were obtained in the current work. The purpose of this comparison is to show how much effect the anion, the nitrate in particular, has on the relaxation properties of the nuclei in the cation and draw conclusions about the ion pairing and solvation effects. Comparison of the data on nitrate, chloride, trimesate, trifluoroacetate (at the same concentration) and the neat amine clearly reveals some trends. First, the C-13 T_1 's in n-butylamine are uniformly larger than in all the different salts. This reinforces the conclusion that the ammonium ion is an effective anchoring group which restricts the molecular motion including that of the end CH_3 group evident in all the n-butylammonium ions. The C-13 relaxation times (T_1 's) in the nitrate are significantly larger, suggesting that the intermolecular interactions are weaker and the molecular motions faster, relatively. Presumably, this is due to less hydrogen-bonding and ion solvation effects in the nitrate. That would also mean a greater degree of ion pairing as was already suggested by the lack of concentration effect.

NOE Measurements

Spin-lattice relaxation can take place by several mechanisms but for protonated carbons, the magnetic dipole-dipole interaction constitutes the dominant mechanism. Measurement of the NOE often provides confirmation, since the maximum possible value (2.98) would be realized only if the dipolar relaxation mechanism operates almost exclusively. The NOE values measured and included in tables 1, 2, and 3 are all clearly close to the maximum within experimental error, confirming that the relaxation mechanism is through dipolar interaction between the C-13's and the attached protons. Other mechanisms including nitrogen-14 quadrupolar relaxation seem to play a negligible role. However, the NOE's observed with added Cu^{++} ions and EDTA (table 5) were substantially lower because of the expected paramagnetic relaxation. In these cases, the T_1 's were so significantly smaller, those with EDTA being smaller than the ones with Cu^{++} ions. The latter may be due to a small contribution of quadrupolar relaxation by the nitrogens in EDTA caused by fluctuating electric fields.

Activation Energies for Molecular Rotations

To determine the energy barriers to the molecular reorientations in the electrolyte solutions, the activation energies were measured in two cases from the Arrhenius plots. In n-butylamine nitrate (NBAN), the activation energies from the T_1 's of all four carbons were in the range, 14.55 ± 0.9 kJ/mole (table 5, last line), while in TMAN, at both concentrations studied, the activation energies were about 10 kJ/mole. Analogous to the case of T_1 's, the activation energies were found to be independent of concentration. For a small molecule freely tumbling in solution, the energy barrier was estimated to be 10 kJ/mole (ref 4). The difference between TMAN and NBAN is not surprising because NBAN, with a larger mass and chain length, may need more energy for the molecular reorientations. The chloride at 1.95 moles/l shows the same activation energy as for the nitrate. The low figure for the chloride at one mole/l concentration is inconsistent with the others and, therefore, suspect in accuracy.

CONCLUSIONS

In summary, in the alkylamine nitrates studied, the C-13 spin-lattice relaxation mechanism is essentially due to dipolar interactions with the attached protons. A general lack of concentration dependence is puzzling and possibly implies the ion pairing effects of the nitrates. The charge carrying ammonium ion sites seem to be good anchoring groups presumably due to solvation effects. The C-13 T_1 's in the NBAN are significantly larger than in the other n-butylammonium salts, perhaps due to ion pairing. The activation energies for the molecular rotations are in the normal range expected for small molecule freely tumbling in solution.

The carbon-13 spin-lattice relaxation measurements in the alkylammonium nitrates were not sufficiently informative in terms of molecular association and ion-clustering effects. As anticipated early in these studies, one must pay

closer attention to the charge sites, both cationic and anionic, through the measurement of nitrogen spin-lattice relaxation times. This can only be done by employing nitrogen-15 labeled samples because the quadrupolar nitrogen-14 nucleus lacks the required sensitivity. Besides, nitrogen-15 T_1 studies would also enable investigation of interactions with hydroxylammonium nitrate which will be N-15 labeled. In each case, the spin-lattice relaxation of the nitrate-nitrogen should furnish valuable information about the role of the nitrate ion. Nitrogen-15 studies have been initiated at ARDEC and will be covered in a future report.

Table 1. Carbon-13 spin-lattice relaxation times (T_1) and nuclear Overhauser enhancements (NOE) observed in aqueous solutions of IPAN, TEAN, and TMAN

Sample	Concentration (moles/l)	Temperature (°C)	C-1		C-2	
			T_1 (sec)	NOE	T_1 (sec)	NOE
IPAN	0.4	20	6.3 ± 0.3	3.2	3.6 ± 0.2	2.8
$(^2\text{CH}_3)_2\text{}^1\text{CHNH}_3^+\text{NO}_3^-$	4.3	20	7.8 ± 0.6	2.7	3.8 ± 0.2	2.8
TEAN	0.33	20	1.2 ± 0.50	-	1.5 ± 0.08	2.6
$(\text{HOCH}_2\text{}^1\text{CH}_2)_3 - \text{NH}^+ - \text{NO}_3^-$	0.33	50	2.4 ± 0.10	-	2.8 ± 0.10	-
	3.60	20	1.1 ± 0.05	2.9	1.3 ± 0.08	2.9
TMAN	0.57	20	8.4 ± 0.25	2.7		
$(^1\text{CH}_3)_3\text{NH}^+\text{NO}_3^-$	0.57	50	12.2 ± 0.30	-		
	3.58	20	8.8 ± 0.10	2.7		

Table 2. Carbon-13 spin-lattice relaxation times (T_1) and nuclear Overhauser enhancements (NOE's) observed in isopropyl-, triethanol- and trimethylamines and their aqueous solutions

Sample	Concentration (moles/l)	Temperature (°C)	C-1		C-2	
			T_1 (sec)	NOE	T_1 (sec)	NOE
$(\text{CH}_3)_2\text{CHNH}_2$	Neat	10	28.2 ± 0.4	2.4	13.9 ± 0.2	2.7
Aqueous solutions	1.0	38	16.7 ± 0.6	2.8	9.2 ± 0.2	2.9
	5.87	38	13.3 ± 0.3	3.0	6.8 ± 0.1	2.9
	10.0	38	15.2 ± 0.2		7.6 ± 0.1	
$(\text{HOCH}_2\text{CH}_2)_3\text{N}$	Neat	38	0.16 ± 0.01	2.6	0.12 ± 0.01	2.4
Aqueous solutions	1.0	38	2.2 ± 0.05	2.6	1.66 ± 0.4	2.8
	5.0	38	0.49 ± 0.01	2.9	0.41 ± 0.01	3.1
$(\text{CH}_3)_3\text{N}$	Neat	0	23.1 ± 0.6	2.5		
Aqueous solutions	1.0	38	5.27 ± 0.14	-		
	6.1	38	4.2 ± 0.04	2.6		

Table 3. Carbon-13 spin-lattice relaxation times (T_1) and NOE's of IPAN, TEAN, and TMAN in the presence of HAN

<u>AAN</u> <u>(mmoles)</u>	<u>HAN</u> <u>(mmoles)</u>	<u>Water</u> <u>(mmoles)</u>	<u>C-1</u>		<u>C-2</u>	
			<u>T_1(sec)</u>	<u>NOE</u>	<u>T_1(sec)</u>	<u>NOE</u>
IPAN 3.4	12.9	23.2	3.2 \pm 1.4	2.8	2.0 \pm 0.1	2.8
TEAN 3.9	20.9	25.2	0.3 \pm 0.05	2.9	0.3 \pm 0.01	2.9
TMAN 4.4	20.1	24.9	3.1 \pm 0.1	2.8		

Table 4. Comparison of the carbon-13 spin-lattice relaxation times (T_1) in n-butylamine and some of its salts in aqueous solution

Anion	Concentration (moles/l)	Spin-lattice relaxation time, T_1 (sec)			
		C-1	C-2	C-3	C-4
(NO ₃ ⁻) ^a	1.12	8.3	9.8	10.6	10.3
(Cl ⁻) ^b	1.0	3.7	5.7	7.3	8.4
Trimesate ^{b,c}	0.33	3.2	3.9	4.9	6.3
Trimesate ^{b,c}	1.0	1.1	1.6	2.0	3.6
(CF ₃ CO ₂ ⁻) ^d	0.27	5.0	5.2	5.8	6.3
(CF ₃ CO ₂ ⁻) ^d	0.54	4.6	4.7	6.2	6.6
(CF ₃ CO ₂ ⁻) ^d	1.08	3.8	4.3	5.0	5.0
None ^{d,e}	-	13.4	13.4	15.0	12.1

^a Measurements were made at 38°C since the data from the literature (see footnotes b and c) were obtained as that temperature.

^b From reference 8.

^c 1, 3, 5-benzenetricarboxylate.

^d From reference 8.

^e n-butylamine neat.

Table 5. Carbon-13 spin-lattice relaxation times (T_1 's) and NOE's in aqueous solutions of NBAN as a function of concentration, temperature and added Cu(II) ions and EDTA

Sample	Concentration moles/l	Temperature °C	C-1	C-2	C-3	C-4
NBAN	0.41	25	$T_1 = 6.0 \pm 0.5$	8.0 ± 0.4	8.7 ± 0.2	7.2 ± 0.6
	0.99	25	$T_1 = 4.4 \pm 0.2$ NOE = 2.45	5.3 ± 0.3 2.59	6.4 ± 0.4 2.54	6.2 ± 0.7 2.76
	1.03	25	$T_1 = 5.7 \pm 0.1$	6.3 ± 0.3	6.2 ± 0.3	7.1 ± 0.5
	1.12	25	$T_1 = 6.3 \pm 0.1$	7.1 ± 0.3	8.7 ± 0.2	8.2 ± 0.3
	1.12	38	$T_1 = 8.3 \pm 0.4$	9.8 ± 0.2	10.6 ± 0.2	10.3 ± 0.3
	3.95	25	$T_1 = 4.2 \pm 0.1$	5.1 ± 0.2	5.7 ± 0.1	6.1 ± 0.3
NBAN + CuCl ₂	$\begin{cases} 0.99 \\ 0.05 \end{cases}$	25	$T_1 = 2.1 \pm 0.1$ NOE = 1.43	2.8 ± 0.4 2.0	3.1 ± 0.7 1.72	2.8 ± 0.3 1.67
NBAN + CuCl ₂ + EDTA	$\begin{cases} 0.99 \\ 0.05 \\ 0.05 \end{cases}$	25	$T_1 = 1.1 \pm 0.1$ NOE = 1.14	1.3 ± 0.1 1.11	1.6 ± 0.2 1.18	1.5 ± 0.1 1.42
NBAN	1.12		$E_a = 14.2 \pm 0.6$ (kJ/mole)	13.7 ± 0.9	15.0 ± 0.7	15.3 ± 0.4

Table 6. Energies of activation for molecular reorientation of trimethylammonium ion as a function of concentration, with nitrate and chloride as anions, derived from the temperature dependence of the carbon-13 spin-lattice relaxation times (T_1 's)

<u>Cation</u>	<u>Anion</u>	<u>Concentration (moles/l)</u>	<u>E_a (kJ/mole)</u>
$(CH_3)_3NH^+$	NO_3^-	1.06	10.5 ± 0.8
$(CH_3)NH^+$	NO_3^-	2.06	10.5 ± 0.6
$(CH_3)_3NH^+$	Cl^-	1.0	4.1 ± 0.4
$(CH_3)_3NH^+$	Cl^-	1.95	8.9 ± 0.5

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